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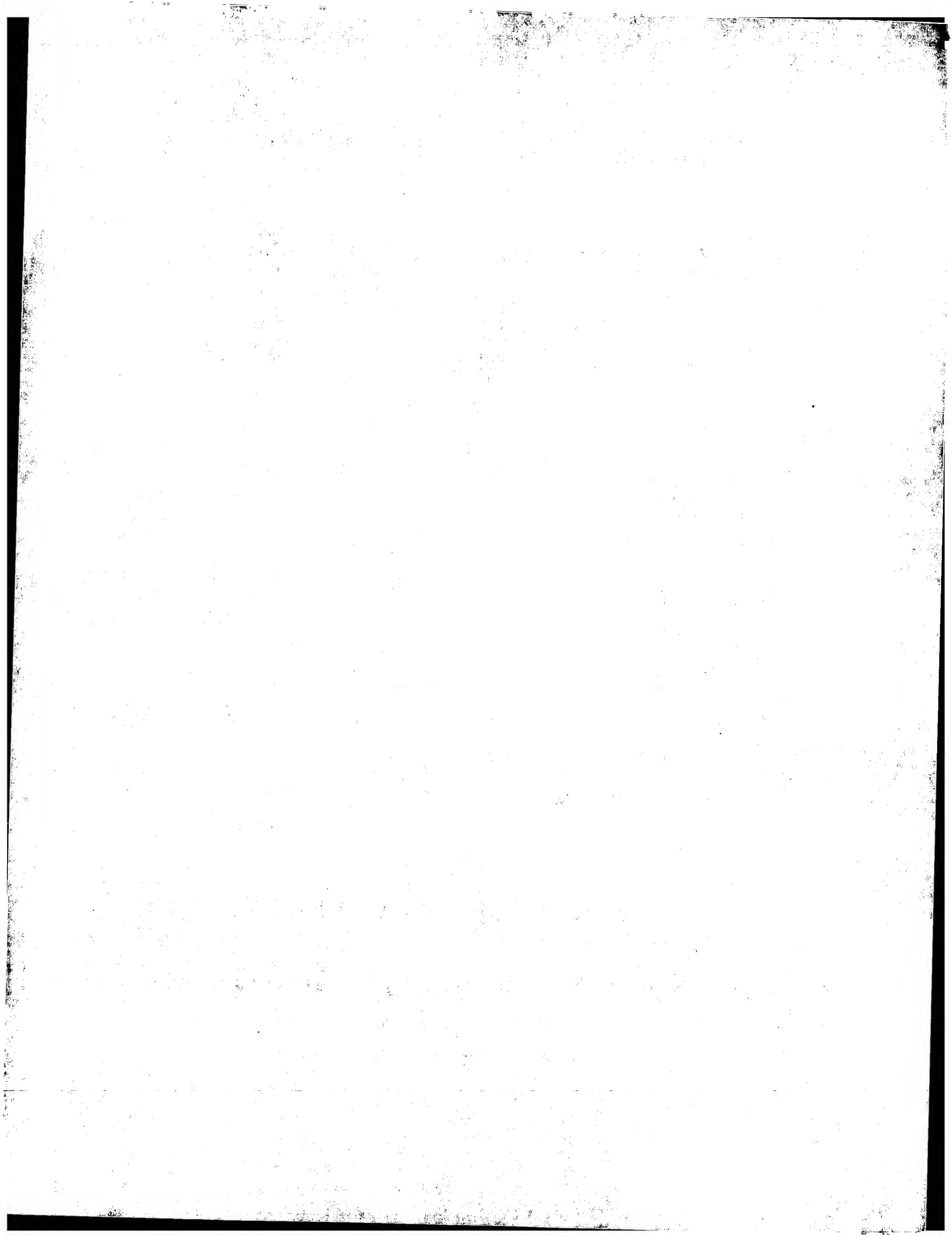
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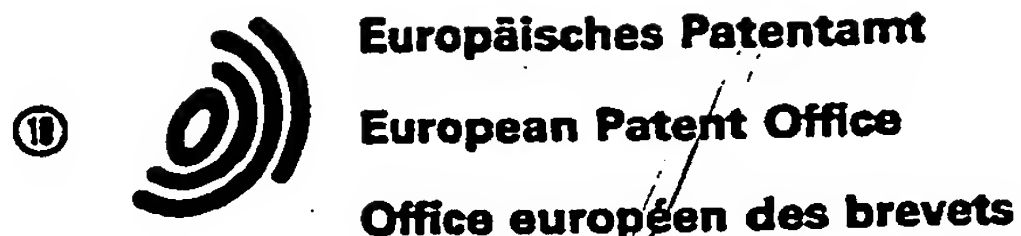
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Description

This invention relates to a constrained-layer construction comprising a stiff layer of substrate and a layer of viscoelastic polymer that is useful to dissipate or damp the destructive and undesirable aspects of vibration. In another aspect, it relates to a process for using a vibration-damping constrained-layer construction in high temperature applications.

It has long been known that the vibration of component parts of devices and structure that vibrate under the influence of an applied internal or external force can be substantially reduced by the attachment of a layer of viscoelastic material. It is particularly useful to provide a laminate of one or more metal sheets and one or more layers of viscoelastic materials (i.e., a constrained-layer construction) to the component part. A large number of viscoelastic materials have been suggested for this purpose. For example, U.S. Patent No. 3,640,836 discloses a vibration-damping laminate in which the viscoelastic layer is a polymer comprised of ethylene, vinyl acetate and acrylic and/or methacrylic acid. U.S. Patent No. 3,847,726 discloses a viscoelastic adhesive composition of a polyepoxide, a polyether amine, a heterocyclic amine, and a phenol useful as vibration-damping material over a -25 to $+60^{\circ}\text{C}$ range. Such compositions, however, are not effective for vibration-damping over prolonged periods of time at elevated temperatures.

U.S. Patent No. 3,941,640 discloses a high temperature operational gasket of asbestos containing a minimum amount of binder that also serves as a vibration-damper. A laminate of asbestos-reinforced bitumen and a metal layer is taught as being especially suitable for noise reduction of internal combustion engine casing parts in U.S. Patent No. 4,048,366. Such vibration-damping materials containing asbestos, a known carcinogen, are undesirable, however.

U.S. Patent No. 3,537,717 discloses a damped ski and method of making utilizing a viscoelastic layer suitable for low temperature use, e.g. -25°C to $+5^{\circ}\text{C}$.

U.S. Patent No. 4,223,073 discloses a vibration-damping composite containing a viscoelastic cyanurate polymer. Although high temperature vibration-damping is taught by the use of these composites, the process for their production is tedious, requiring curing temperatures up to 200°C for several hours, and utilizes sulfuric acid or another strong acid as a catalyst (see U.S. Patent No. 3,803,088, col. 4, lines 9-15) which can cause undesirable side reactions.

In one aspect the invention provides a constrained-layer construction for damping vibrations in solid articles at a temperature of at least 50°C , said construction comprising a substrate having a stiffness relative to stainless steel of at least 0.40 and bearing a continuous layer of a copolymer having a thickness of 0.01 mm to 100 mm, said copolymer having a storage modulus of at least 1×10^7 dynes/cm² ($1 \text{ dyne} = 10^{-5} \text{ N}$) and a loss tangent above 0.5 at 100°C and 1000 Hz, said copolymer being the reaction product of a mixture comprising:

a) 25 to 75 weight percent of an acryloyl or methacryloyl derivative of at least one nucleophilic group-substituted oligomer being selected from the group consisting of polyoxyalkylene, poly(perfluoro-oxyalkylene), polyester, polyolefin, polyacrylate, polyamide, and polysiloxane oligomers, said oligomer having a glass transition temperature of less than 25°C and a molecular weight per oligomer of 600 to 20,000, and

b) 75 to 25 weight percent of a copolymerizable monomer whose homopolymer has a glass transition temperature of at least 50°C .

In another aspect the invention provides a process for damping the vibration of a vibrating solid article at temperatures above 50°C , said process comprising the steps:

a) providing a constrained-layer construction as defined above wherein said viscoelastic copolymer is admixed with an effective amount of a free-radical generator; and
b) affixing said constrained-layer construction onto said solid article.

Preferably, $\tan \delta$ is greater than 0.7.

Preferred features of the invention are defined in the dependent claims.

Properties of vibration-damping materials are described in the literature. Nielsen, L. E., "Mechanical Properties of Polymers", pages 162-165, Reinhold Publishing Corp., New York (1965) discloses that materials possessing the maximum vibration-damping capability have storage moduli, G' , greater than 10^7 dynes/cm² but less than 10^{10} dynes/cm² at the use temperature. Furthermore, Rosen, S. L., "Fundamental Principles of Polymeric Materials for Practicing Engineers", pages 222-227, Barnes & Noble Inc., New York, (1971), shows that it is desirable for a vibration-damping material to have both a storage modulus and a loss tangent with values as high as possible.

Yerges, L. F., "Sound, Noise, and Vibration Control", Van Nostrand Reinhold Company, New York, pages 68 and 69, (1969) notes that useful damping materials exhibit decay rates from as low as 5 to 80 dB/sec (decibels/second), and from 1/2 to 20 percent of critical damping. ("Critical" damping is the damping necessary to just prevent oscillation).

As is known in the art, the most efficient use of the damping material occurs if the material is sandwiched between the panel to be damped and a relatively stiff layer, such as thin sheet metal. This forces the damping material into shear as the panel vibrates, dissipating substantially more energy than when the material acts simply in extension and compression.

Solid articles comprising the viscoelastic copolymers of the invention may be prepared by either of two processes. In a first process, a layer of the polymerizable mixture is coated onto a release liner, the mixture

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polymerized, and the layer of resulting copolymer transferred to a substrate and adhered thereto, thereby providing a constrained-layer construction. In the second process, a layer of the polymerizable mixture is coated directly onto a substrate and the mixture polymerized *in situ* thereby also providing a constrained-layer construction. The constrained-layer construction may then be mechanically (e.g., as by bolting) or adhesively affixed to the solid article that requires vibration damping. When the solid article subsequently vibrates under the influence of an internal or external applied force, vibration in the solid article is damped.

As used in this application:

"nucleophilic group" means a group having a pair of unshared electrons such as hydroxyl, amino, and thiol groups;

"free-radical generator" means both thermally and photochemically activatable free-radical initiators and sensitizers;

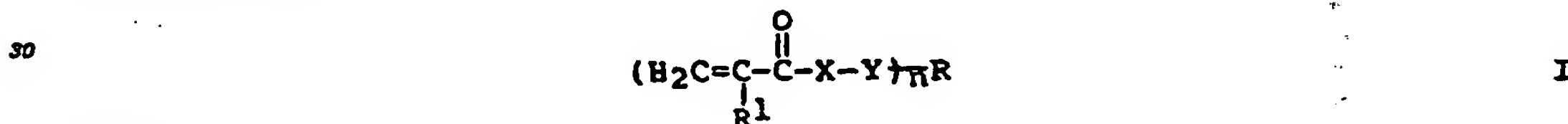
"activating radiation" means electromagnetic (e.g., visible or ultraviolet) or ionizing (e.g., high energy electrons) radiation;

"storage modulus", designated by convention as G' , is a measure of the elastic stress-strain response to an applied force of a material when measured in shear; and

"solid article" means a portion or the whole of a structure, e.g., it may be a thermo print head of a computer, a turbine or a guide vane of a jet engine, a component of an engine or a transmission of an automobile or other machinery, a building, or a gas tank.

The polymerizable mixtures suitable for preparing the thermally-resistant, viscoelastic polymers of use in vibration-damping constructions of the invention may be made by mixing together 25 to 75 percent by weight of one or more acryloyl or methacryloyl derivatives of a nucleophilic group-substituted oligomer, wherein the nucleophilic group may be pendant or terminal but preferably is terminally substituted, that has a T_g of less than 25°C and one to six hydroxyl, amino, or thiol groups per oligomer with a corresponding 75 to 25 percent by weight of one or more free-radically polymerizable monomers whose homopolymers has a T_g of at least 50°C . Optionally, other supplementary components, to be described below, can be added to the polymerizable mixture to provide additional desired characteristics.

Preferably, the acryloyl and methacryloyl derivatives of oligomers of use in the viscoelastic polymer have the formula:



wherein:

R is the residue of the nucleophilic group-substituted oligomer after removal of n hydroxyl, amino or thio groups;

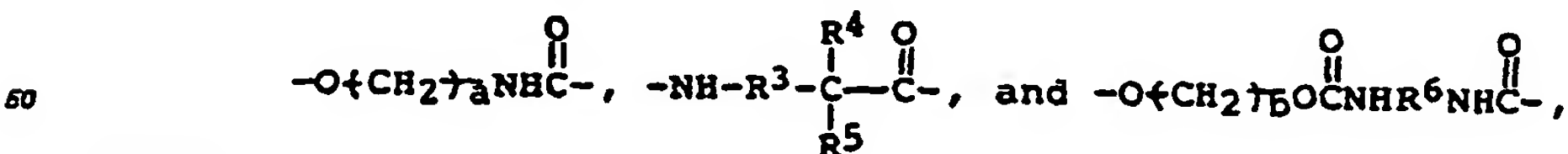
n is the valence of R having a value of at least one;

Y is selected from —O—, —S—, and



in which R^2 is a) hydrogen, or b) a hydrocarbyl group selected from (1) an alkyl or cycloalkyl group having 1 to 12 carbon atoms optionally substituted by a cyano, hydroxyl, or alkoxy group having 1 to 4 carbon atoms, or (2) an aryl or aralkyl group having 6 to 12 carbon atoms;

X is a divalent connecting group, selected from the group consisting of a covalent bond,



in which:

a and b independently are integers having a value of 2 to 12;

R^3 is a covalent bond, a methylene group, or an ethylene group, the last two of which can be substituted by an alkyl group having 1 to 6 carbon atoms or a phenyl group;

R^4 and R^5 are independently hydrogen, an alkyl group or a cycloalkyl group having 1 to 12 carbon atoms, an aryl or aralkyl group having 6 to 12 carbon atoms, or R^4 and R^5 taken together with the carbon to which they are attached form a 5- to 12-membered carbocyclic ring; and

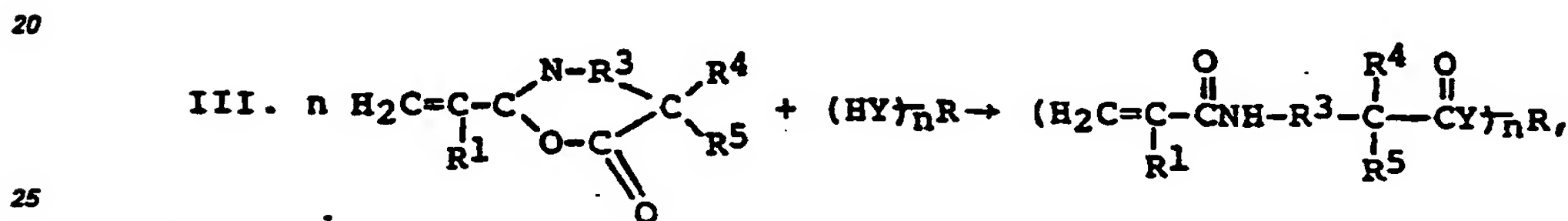
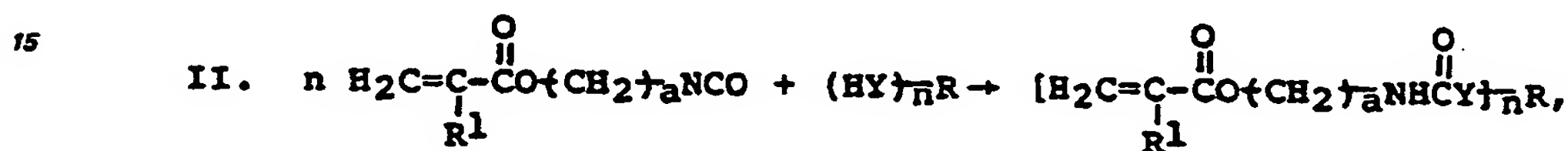
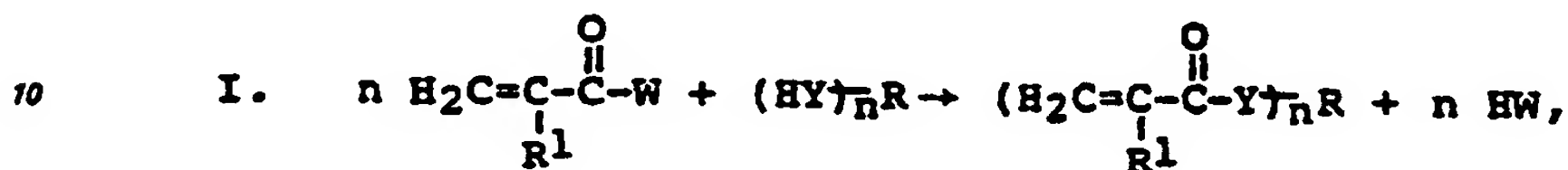
R^6 is an alkyl group or cycloalkyl group having 1 to 15 carbon atoms, or an aryl or aralkyl group having 6 to 15 carbon atoms;

with the proviso that when R^2 is a hydrocarbyl group, then at least one of R^4 and R^5 is hydrogen; and R^1 is hydrogen or methyl.

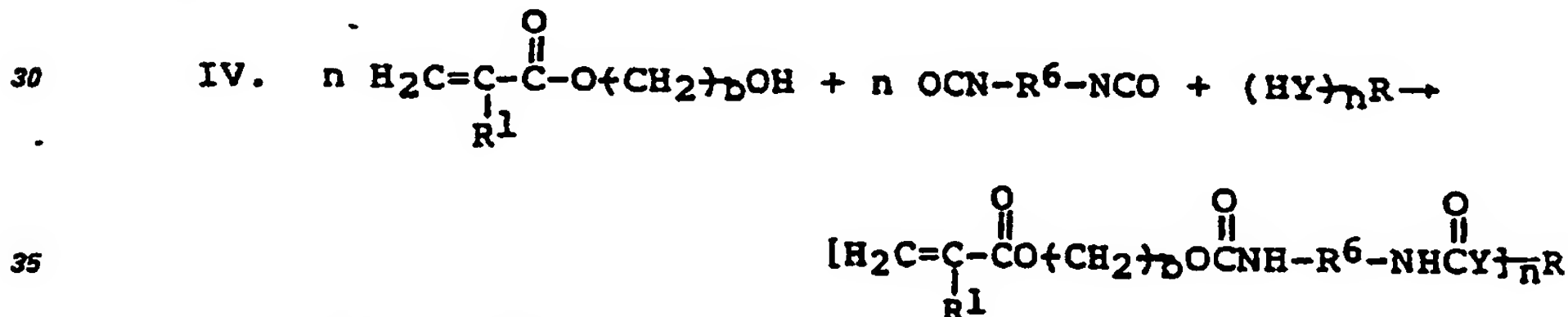
Acryloyl and methacryloyl derivatives of use in the viscoelastic polymers of the invention may be prepared by the reaction of any acryloylating agent with a nucleophilic group-substituted oligomer (i.e., an organic compound having repeating units that is preferably terminally substituted by at least one

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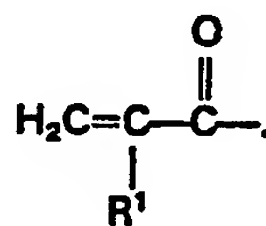
nucleophilic group, i.e., an electron-rich group). Suitable nucleophilic oligomers are those having a molecular weight of 600 to 20,000 and, therefore, from about 10 to about 500 repeating units and 1 to 6 nucleophilic groups per oligomer selected from hydroxyl, amino, and thiol groups. Useful acryloylating agents are acrylic or methacrylic acid, their halides, esters or anhydrides, and preferably their isocyanatoalkyl esters, and most preferably the alkenyl azlactones. Reactions leading to the formation of these functional oligomers proceed according to the equations:



and



in which R, R¹, R³, R⁴, R⁵, R⁶, Y, a, b and n are defined above, and W is halide or OR⁷ in which R⁷ is hydrogen, lower alkyl, phenyl, or



Thus, in accordance with Equation I, acrylic acid or methacrylic acid, their esters, halides, or anhydrides can be caused to react in a well-known metathetical reaction with suitable nucleophilic group-substituted oligomers, to be described below.

Preferably, because no by-products are produced by the reaction, the acryloyl and methacryloyl derivatives of use in the mixture of the invention are prepared in accordance with the reactions of Equation II or Equation III. In accordance with Equation II, the derivatives are prepared by reaction of the nucleophilic group-substituted oligomer with an isocyanatoalkyl acrylate or methacrylate such as, for example, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl acrylate, 4-isocyanatobutyl acrylate, 6-isocyanatohexyl acrylate, 12-isocyanatododecyl acrylate, and the corresponding methacrylates. In accordance with Equation III, the derivatives are prepared by reaction of the nucleophilic group-substituted oligomer and an alkenyl azlactone. The preparation of the alkenyl azlactones is discussed in assignee's U.S. Patent No. 4,304,705, which patent is hereby incorporated herein by reference. Examples of suitable alkenyl azlactones include:

- 2-ethenyl-1,3-oxazolin-5-one,
- 2-isopropenyl-1,3-oxazolin-5-one,
- 2-ethenyl-4,4-dimethyl-1,3-oxazolin-5-one,
- 2-isopropenyl-4,4-pentamethylene-1,3-oxazolin-5-one,
- 2-ethenyl-5,6-dihydro-4H-1,3-oxazin-6-one,
- 2-isopropenyl-5,6-dihydro-5,5-dimethyl-4H-1,3-oxazin-6-one, and

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2-isopropenyl-4,5,6,7-tetrahydro-6,6-dimethyl-1,3-oxazepin-7-one.

Other suitable alkenyl azlactones are described in U.S. Patent No. 4,304,705.

In addition, the acryloyl and methacryloyl derivatives of use in the mixture of the invention are prepared in a two-step sequence as illustrated by Equation IV above. In accordance with Equation IV, the nucleophilic group-substituted oligomer is first reacted with a polyisocyanate to produce an isocyanate functional oligomer having at least one —NCO group. In the second step this isocyanate functional oligomer is reacted with a hydroxyalkyl acrylate or methacrylate. This reaction, where R is polycaprolactone, is described in U.S. Patent No. 3,700,643.

Suitable nucleophilic group-substituted oligomers which can be reacted with acryloylating reactants in accordance with Equations I, II, III, or with a polyisocyanate as in Equation IV to produce the polymerizable derivatives of use in the compositions of the invention can vary widely within the scope of the invention. Particularly useful examples include: 1) polyether polyols such as polyethyleneglycol, polypropyleneglycol and poly-tetramethyleneglycol, and poly(perfluoroether)diols, and the like; 2) polyester polyols such as polycaprolactone polyols, polyneopentyladipate polyols, and the like; 3) polyoxyalkylene polyamines such as the polyethylene- and polypropyleneoxide based mono- and polyamines available from Jefferson Chemical Co., Inc., a subsidiary of Texaco, Inc., under the trade name Jeffamine®; 4) hydroxy- and amino-functional derivatives of polymerized fatty acids, more commonly referred to as "dimer" or "trimer" acid derivatives, such as those sold commercially under the trade designation Kemamine® (Humko Sheffield Chemical); 5) hydroxy- or amino-functional olefin polymers and copolymers such as hydroxy-terminated polybutadienes and amine-terminated butadiene-acrylonitrile copolymers (B.F. Goodrich's HYCAR® ATBN); 6) primary or secondary amino-functional polyamides such as those useful as epoxy curing agents (e.g., Emerez® reactive polyamide resins from Emery Industries, Inc.); 7) polyvinyl alcohol and other hydrolyzed or partially hydrolyzed vinyl acetate homo- and interpolymers; and 8) polysiloxane polyols such as those described in U.S. Patent Nos. 4,098,742; 3,886,865; 3,577,264; and 4,013,698. A particular class of materials useful for preparation of the oligomers of the present invention is a series of polyamides or polyethers of the general structure:



wherein R⁸ is the residue of a mono- or poly-functional carboxylic acid having at least one carboxyl group removed therefrom, R⁹ is a radical of a polyvalent corresponding to a polyether polyamine having a molecular weight of from about 200 to about 10,000, and c and d are independently integers from 1 to 4. These polyamines are conveniently prepared by standard condensation techniques from the appropriate organic acid (or suitable derivative) and excess polyether polyamine such as those described in U.S. Patent Nos. 4,107,061 and 3,257,342.

Suitable free-radically copolymerizable comonomers for use in the polymerizable mixture suitable for preparing the viscoelastic polymers of use in the vibration-damping constructions of the invention are those whose homopolymers have a glass transition temperature of at least 50°C. The glass transition temperature of polymers is well-known in polymer chemistry [see, for example, Brandrup and Immergut, Polymer Handbook, III, pp. 61—73, Interscience Publishers (1967)]. Examples of suitable monomers (and the T_g of their homopolymers) are N-vinylpyrrolidone (86°C), acrylic acid (87°C), N,N-dimethylacrylamide (89°C), styrene (100°C), methyl methacrylate (105°C), isobornyl acrylate (94°C), 2-chlorostyrene (119°C), acrylamide, acrylonitrile (120°C), methacrylonitrile (120°C), and dichlorostyrene (133°C). As described above, the total polymerizable mixture contains at least 25 percent by weight of monomer whose homopolymer has a T_g of at least 50°C, at least 25 percent by weight of the total polymerizable mixture of an acryloyl or methacryloyl derivative of a suitable nucleophilic oligomer, and up to 50 percent by weight of a diluting free-radically polymerizable monomer whose T_g is less than 50°C. Included among such diluting monomers (and the T_g of their homopolymer) are 2-(N-butylcarbonyl)ethyl methacrylate (31°C), butyl methacrylate (20°C), methyl acrylate (6°C), ethyl acrylate (−24°C), and butyl acrylate (−55°C).

It is sometimes desirable to add to the polymerizable mixtures up to about 5 percent by weight of a multiacrylate-functional monomer to enhance the crosslink density of the polymerized mixture. By doing so, viscoelastic polymers, which at a desired temperature and frequency have inadequate storage moduli and/or loss tangents, can be upgraded to polymers having storage moduli and loss tangents that are in the desired range. Suitable multiacrylate-functional monomers include ethylene diacrylate, trimethylolpropane triacrylate, methylenebis(acrylamide), hexanediol diacrylate, divinylbenzene, pentaerythritol tri- and tetraacrylate, 1,3,5-tri(2-methacryloxyethyl)-s-triazine, and the like.

The polymerizable mixtures of use in the invention also may contain up to about ten percent by weight of the mixture of additives (i.e., fillers, reinforcing agents, antioxidants, etc.) normally added to vibration-damping materials. Suitable fillers include ground mica, limestone, stone dust, sand, clay, chopped fiberglass, pigments, and the like. Particularly desirable fillers are the fumed silicas such as Cab-O-Sil® M5, available from Cabot Corporation, that are excellent thickening agents which facilitate the coating operation and improve the substantivity of the coating composition to some substrates. It is also often

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A sufficient amount of each mixture was placed into an aluminum tray having an area of about 20 cm² to provide a layer of 2.5 mm \pm 0.1 mm thickness. Each tray was placed into a chamber under a Sylvania Blacklight F15T8-BLB (an ultraviolet emitting lamp, Sylvania, Inc., division of GTE Corp.) at a distance of 10 cm. The air was displaced from the chamber with nitrogen and the contents of each tray were irradiated for ten minutes. For each mixture, a tough, tear-resistant, flexible, generally almost colorless sheet of viscoelastic polymer was obtained. The storage modulus and loss tangent of the polymers were determined and the results are presented in Table I below.

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TABLE I
Initial Storage Modulus (G') and Loss Tangent (δ) Data

Ex. No.	Acrylated or Methacrylated Oligomer (Parts)	"Monomer"(a) (Parts)	Additive (percent)	Polymer Characteristics	
				G'x10 ⁷ (d)	Tan δ (e)
1	VDM-ED900 (1)	AA (1)	-	4.08	1.26
2	VDM-ED900 (1)	NVP (1)	-	2.30	0.759
3	VDM-D2000 (1)	MM (2)	-	3.53	0.883
4	VDM-D2000 (1)	NVP (2)	-	2.45	0.292
5	VDM-D2000 (1)	AA (1)	-	28.0	0.554
6	VDM-D2000 (1)	AA (1)	TMPA(b) (1)	5.68	1.09
7	VDM-D2000 (1)	AA (1)	TMPA (5)	26.0	0.625
8	VDM-D2000 (3)	AA (1)	-	4.61	0.615
9	VDM-D2000 (1)	DMA (2)	SiO ₂ (c) (8)	5.47	0.83
10	VDM-D2000 (1)	DMA (2)	SiO ₂ (6)	9.0	0.9
11	IEM-CW1450 (1)	DMA (2)	-	3.54	1.32
12	IEM-PCP2000 (1)	DMA (2)	-	8.74	1.35
13	MA-CW1000 (1)	DMA (2)	-	2.28	1.20
14	MA-CW1000 (1)	DMA (3)	-	16.2	1.45

(a) Monomer having a Tg of greater than 50°C; (c) SiO₂ fumed silica (Cab-O-Sil M-5)

AA acrylic acid (d) G' storage modulus in dynes/cm² measured at 100°C and 1000 Hz

NVP N-vinylpyrrolidone (e) Tan δ loss tangent

MM methylmethacrylate

DMA N,N-dimethylacrylamide

(b) TMPA trimethylolpropane triacrylate

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desirable to include within the polymer layer a scrim of thermally-resistant fibers such as fibers of polyester, glass fibers, and particularly, ceramic microfibers.

The viscoelastic polymers of use in the present invention and laminates containing these polymers are prepared according to the steps of either Method I or Method II.

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Method I:

1. coating a release liner with a layer of the polymerizable mixture of the invention,
2. polymerizing the mixture to a viscoelastic polymer layer,
3. transferring the viscoelastic polymer layer from the release liner to a substrate, and
4. adhering the viscoelastic polymer layer to the substrate to form the constrained-layer vibration-damping construction; or

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Method II:

1. coating a substrate with a layer of the polymerizable mixture, and
2. polymerizing the mixture to a viscoelastic polymer layer *in situ* onto the substrate to form the constrained-layer vibration-damping construction.

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In both of the above-described processes, it is preferable to add to the polymerizable mixture free-radical initiator (0.01 to 5 weight percent) to promote polymerization. Suitable free-radical initiators which may be added to produce thermally curable coating mixtures include azo compounds such as azobis(isobutyronitrile), hydroperoxides such as tert-butyl hydroperoxide, peroxides such as benzoyl peroxide or cyclohexanone peroxide, and also include redox catalysts such as the persulfate/bisulfite pair, peroxide/tertiary amine combinations, or other redox couples capable of initiating free-radical polymerizations. Generally, from about 0.01 to 5 percent by weight of thermally activatable initiator based on total polymerizable mixture is used.

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While it is within the scope of this invention to utilize thermally polymerizable mixtures as described above, an additional aspect, which in many instances becomes a preferred embodiment, of the invention is with mixtures that are polymerizable by activating radiation. An excellent discussion of different forms of activating radiation can be found in W. J. Moore's text entitled "Physical Chemistry", 3rd Edition, p. 819, Prentice Hall (1964). When the source of activating radiation is electromagnetic, a sensitizer or photoinitiator is preferably added to the mixture. Any of the common sensitizers or photoinitiators may be utilized such as benzophenone, benzophenone/amine combinations, benzoin, benzoin ethers and their derivatives such as the dimethyl ketal of benzil. Additional listings of sensitizers and photoinitiators which are useful in the invention may be found in J. F. Rabek, *Photochemistry and Photobiology*, 7, 5 (1968) and in G. Oster and N. Yang, *Chem. Rev.*, 68, 125 (1968). These sensitizers are generally incorporated at about 0.01 to about 5.0 percent by weight, although higher levels may be utilized.

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Since the viscoelastic polymer generally has adhesive properties, the polymer can usually be adhered to a stiff layer or substrate without the use of an adhesive. It is sometimes desirable, however, to use a thin layer (e.g., 20—50 μm) of high-modulus adhesive, such as an acrylic adhesive or an epoxy adhesive, to bond the polymer to a solid article which can be, for example, an oil pan, a valve cover, or a transmission housing.

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For most applications, the layer of viscoelastic polymer is a coating having a thickness of at least 0.01 mm up to about 100 mm, preferably 0.025 to 100 mm, and most preferably 0.05 to 100 mm. The coating can be applied by any of the techniques known in the art such as by spray, dip, knife, or curtain coating.

As mentioned above, a stiff layer of substrate is an essential part of the constrained-layer vibration-damping constructions of the present invention. A suitable material for a substrate has a stiffness of 0.40 (relative to stainless steel) as defined in "Handbook of tables for Applied Engineering Science", ed. Bolz, R.E. et al., CRC Press, Cleveland, OH, page 130 (1974). The desired stiffness of the substrate is varied by adjusting the thickness of the layer, for example from about 25 micrometers to 5 centimeters, depending on the modulus of the substrate. Examples of suitable materials include metals such as iron, steel, nickel, aluminum, chromium, cobalt and copper, and alloys thereof and stiff polymeric materials such as polystyrene, polyvinylchloride, polyurethane, polycarbonate, and polyepoxide, glass fiber-reinforced plastics such as glass fiber, ceramic fiber and metal fiber-reinforced polyester, glasses, and ceramics.

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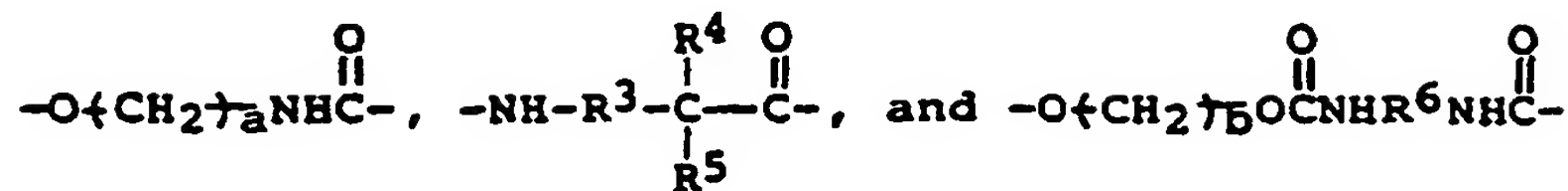
To be satisfactory as a high temperature-resistant vibration-damping material for applications in the automotive, aerospace, and computer industries, a polymer must possess a loss tangent, $\tan \delta$, above 0.5, preferably above 0.7, and a storage modulus above 1×10^7 dynes/cm², and preferably between 1×10^7 and 5×10^8 dynes/cm² or higher at temperatures above 50°C, preferably above 75°C, and most preferable in the range of 100—150°C, and stability against change of these characteristics following exposure of the polymer to air at 100°C for at least 1000 hours. Procedures for determining the loss of tangent and storage modulus of materials are well known in polymer physics and are described, for example, by Miles, *J. Appl. Phys.*, 33 (4), 1422—1428 (1962). Measurements reported herein were made using a Dynamic Shear Rheometer, Model CSR-1, from Melabs of Palo Alto, California, that had been modified to ensure parallel alignment of the driver and pick-up piezoelectric transducers. Stress on the sample and phase shift were read directly using state of the art amplifiers and a phase network analyzer to monitor the output electrical signal.

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Objects and advantages of this invention are further illustrated by the following examples, but the

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5 wherein:

a and b independently are integers having a value of 2 to 12;

R³ is a covalent bond, a methylene group, or an ethylene group, the last two of which can be substituted by an alkyl group having 1 to 6 carbon atoms or a phenyl group;

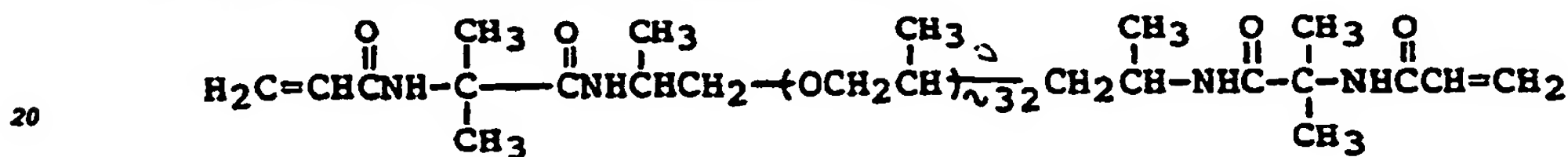
10 R⁴ and R⁵ are independently hydrogen, an alkyl group or a cycloalkyl group having 1 to 12 carbon atoms, an aryl or aralkyl group having 6 to 12 carbon atoms, or R⁴ and R⁵ taken together with the carbon to which they are attached form a 5- to 12-membered carbocyclic ring; and

R⁶ is an alkyl group or cycloalkyl group having 1 to 15 carbon atoms, or an aryl or aralkyl group having 6 to 15 carbon atoms;

with the proviso that when R² is a hydrocarbonyl group, then at least one of R⁴ and R⁵ is hydrogen; and

15 R¹ is hydrogen or methyl.

3. The construction according to any preceding claim wherein said oligomer has the formula:



4. The construction according to any preceding claim wherein said copolymerizable monomer is selected from the group consisting of methyl methacrylate and N,N-dimethylacrylamide.

25 5. The construction according to any preceding claim further comprising up to 50 percent by weight of a diluting free-radically polymerizable monomer having a T_g less than 50°C.

6. The construction according to any preceding claim wherein said substrate is selected from the group consisting of metals, stiff polymeric materials, glass fiber-reinforced plastics, ceramic fiber, glass, ceramics, and metal fiber-reinforced polyester.

30 7. A process for damping the vibration of a vibrating solid article at temperatures above 50°C, said process comprising the steps:

a) providing a constrained-layer construction according to any preceding claim, wherein said viscoelastic copolymer is admixed with an effective amount of a free-radical generator; and

b) affixing said constrained-layer construction onto said solid article.

Patentansprüche

40 1. Konstruktion mit unter Zwangsbedingungen stehender Schicht zum Dämpfen von Schwingungen in festen Gegenständen bei einer Temperatur von mindestens 50°C, mit einem Substrat, das auf nichtrostenden Stahl bezogen eine Steifheit von mindestens 0,40 hat und das eine aus einem Copolymer bestehende, ununterbrochene Schicht in einer Stärke von 0,01 bis 100 mm aufweist, wobei das Copolymer einen Speichermodul von mindestens 1 × 10⁷ dyn/cm² und eine Verlusttangente über 0,5 bei 100°C und 1000 Hz hat und das Reaktionsprodukt eines Gemisches ist, das enthält:

45 a) 25 bis 75 Gew.% eines Acryl- oder Methacryl-derivats mindestens eines mit einer nukleophilen Gruppe substituierten Oligomers, das aus der Gruppe ausgewählt ist, die aus den Polyoxyalkylen-, Poly(perfluoro-oxyalkylen)-, Polyester-, Polyolefin-, Polyacrylat-, Polyamid- und Polysiloxanoligomeren besteht und das eine Einfriertemperatur unter 25°C und ein Molekulargewicht von 600 bis 20 000 pro Oligomer hat und

50 b) 75 bis 25 Gew.% eines copolymerisierbaren Monomers, dessen Homopolymer eine Einfriertemperatur von mindestens 50°C hat.

2. Die Konstruktion mit unter Zwangsbedingungen stehender Schicht nach Anspruch 1, dadurch gekennzeichnet, daß das genannte Derivat eines Oligomers die Formel

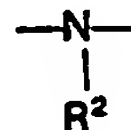


in der

60 R der nach dem Abspalten von n Hydroxyl-, Amino- oder Thiol-gruppen verbleibende Rest des mit einer nukleophilen Gruppe substituierten Oligomers ist,

n die Wertigkeit von R ist und mindestens den Wert eins hat;

Y aus —O—, —S— und



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Examples 15—18

Selected viscoelastic polymers were subjected to heat aging at 100°C in air for 1000 hours, after which the storage modulus and loss tangent were redetermined. The data are presented in Table II below.

TABLE II

Storage Modulus (G') and Loss Tangent (δ) Data After Heat Aging

Ex. No.	Composition of Example	Polymer Characteristics	
		G'*	Tan δ
15	1	1.19	1.695
16	2	4.23	0.857
17	3	3.31	1.253
18	6	15.1	0.839

* G' storage modulus in dynes/cm² x 10⁻⁷ measured at 100°C and 1000 Hz

The data in Tables I and II show that mixtures of an acryloylated or methacryloylated oligomer and methyl methacrylate or dimethylacrylamide provide viscoelastic polymer having excellent characteristics for damping vibration at elevated temperatures.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

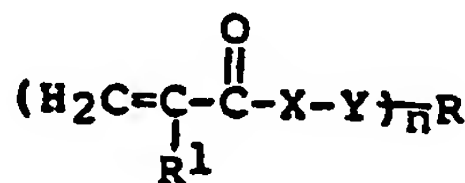
Claims

1. A constrained-layer construction for damping vibrations in solid articles at a temperature of at least 50°C, said construction comprising a substrate having a stiffness relative to stainless steel of at least 0.40 and bearing a continuous layer of a copolymer having a thickness of 0.01 mm to 100 mm, said copolymer having a storage modulus of at least 1×10^7 dynes/cm² and a loss tangent of 0.5 at 100°C and 1000 Hz, said copolymer being the reaction product of a mixture comprising:

a) 25 to 75 weight percent of an acryloyl or methacryloyl derivative of at least one nucleophilic group-substituted oligomer being selected from the group consisting of polyoxyalkylene, poly(perfluoro-oxyalkylene), polyester, polyolefin, polyacrylate, polyamide, and polysiloxane oligomers, said oligomer having a glass transition temperature of less than 25°C and a molecular weight per oligomer of 600 to 20,000, and

b) 75 to 25 weight percent of a copolymerizable monomer whose homopolymer has a glass transition temperature of at least 50°C.

2. The constrained-layer construction according to claim 1 wherein said derivative of an oligomer has the formula

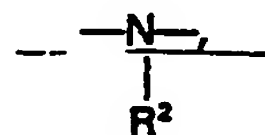


wherein

R is the residue of the nucleophilic group-substituted oligomer after removal of n hydroxyl, amino or thio groups;

n is the valence of R having a value of at least one;

Y is selected from —O—, —S—, and



In which R² is a) hydrogen, or b) a hydrocarbonyl group selected from (1) an alkyl or cycloalkyl group having 1 to 12 carbon atoms optionally substituted by cyano, hydrogen, or alkoxy group having 1 to 4 carbon atoms, or (2) an aryl or aralkyl group having 6 to 12 carbon atoms;

X is a divalent connecting group selected from the group consisting of a covalent bond,

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b) 75 à 25% en poids d'un monomère copolymérisable dont l'homopolymère a une température de transition vitreuse d'au moins 50°C.

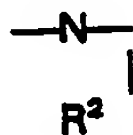
2. Structure à couche emprisonnée selon la revendication 1, dans laquelle ledit dérivé d'oligomère répond à la formule



dans laquelle:

R est le reste de l'oligomère substitué par un ou plusieurs groupes nucléophiles après élimination de n groupes hydroxyle, amino ou thiol;
n est la valence de R qui a une valeur d'au moins un;
Y est choisi parmi, —O—, —S— et

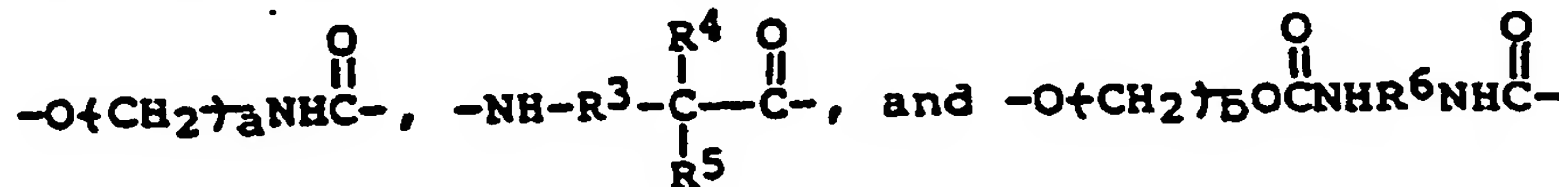
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où R² est a) un atome d'hydrogène ou b) un groupe hydrocarbyle choisi parmi (1) un groupe alkyle ou cycloalkyle ayant de 1 à 12 atomes de carbone, facultativement substitué par un groupe cyano, un atome d'hydrogène ou un groupe alcoxy ayant de 1 à 4 atomes de carbone, ou (2) un groupe aryle ou aralkyle ayant de 6 à 12 atomes de carbone;

X est un groupe connecteur divalent choisi parmi l'ensemble constitué par une liaison covalente

25



30 où

a et b sont indépendamment des nombres entiers ayant pour valeur 2 à 12;

R³ est une liaison covalente, un groupe méthylène, un groupe éthylène, ces deux derniers pouvant être substitués par un groupe alkyle ayant de 1 à 6 atomes de carbone ou un groupe phényle;

R⁴ et R⁵ sont indépendamment un atome d'hydrogène, un groupe alkyle ou un groupe cycloalkyle ayant de 1 à 12 atomes de carbone, un groupe aryle ou aralkyle ayant de 6 à 12 atomes de carbone, R⁴ et R⁵, considérés ensemble avec l'atome de carbone auquel ils sont liés, pouvant former un cycle carbocyclique de 5 à 12 sommets; et

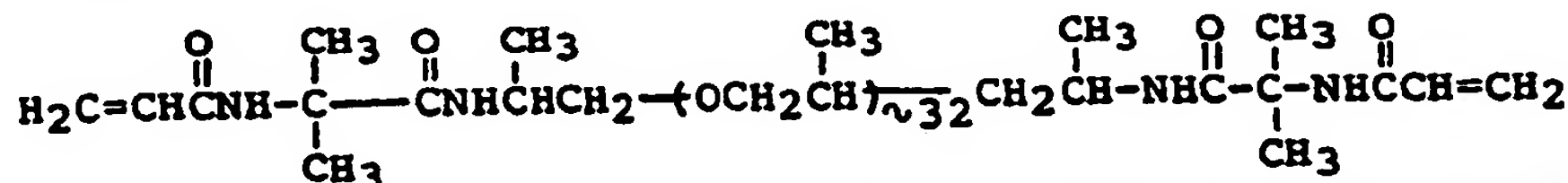
R⁶ est un groupe alkyle ou un groupe cycloalkyle ayant de 1 à 15 atomes de carbone, ou un groupe aryle ou aralkyle ayant de 6 à 15 atomes de carbone;

sous réserve que lorsque R² est un groupe hydrocarbyle, au moins un des R⁴ et R⁵ soit un atome d'hydrogène; et

R¹ est un atome d'hydrogène ou un groupe méthyle.

3. Structure selon l'une quelconque des revendications précédentes, dans laquelle ledit oligomère a pour formule:

45



50

4. Structure selon l'une quelconque des revendications précédentes, dans laquelle ledit monomère copolymérisable est choisi parmi l'ensemble constitué par le méthacrylate de méthyle et le N,N-diméthylacrylamide.

5. Structure selon l'une quelconque des revendications précédentes comprenant en outre jusqu'à 50% en poids d'un monomère diluant polymérisable par mécanisme radicalaire ayant une Tg inférieure à 50°C.

6. Structure selon l'une quelconque des revendications précédentes, dans laquelle ledit substrat est choisi dans l'ensemble constitué par les métaux, les matières polymères rigides, les plastiques renforcés de fibres de verre, les fibres céramiques, le verre, les céramiques et les polyesters renforcés de fibres métalliques.

7. Procédé pour atténuer les vibrations d'un article solide vibrant à des températures supérieures à 50°C, ledit procédé comprenant les stades consistant à:

a) faire appel à une structure à couche emprisonnée selon l'une quelconque des revendications précédentes, dans laquelle ledit copolymère viscoélastique est mélangé suivant une quantité efficace d'un générateur de radicaux libres; et

b) fixer ladite structure à couche emprisonnée sur ledit article solide.

